Alternative, Green Processes for the Precision Cleaning of Aerospace Hardware

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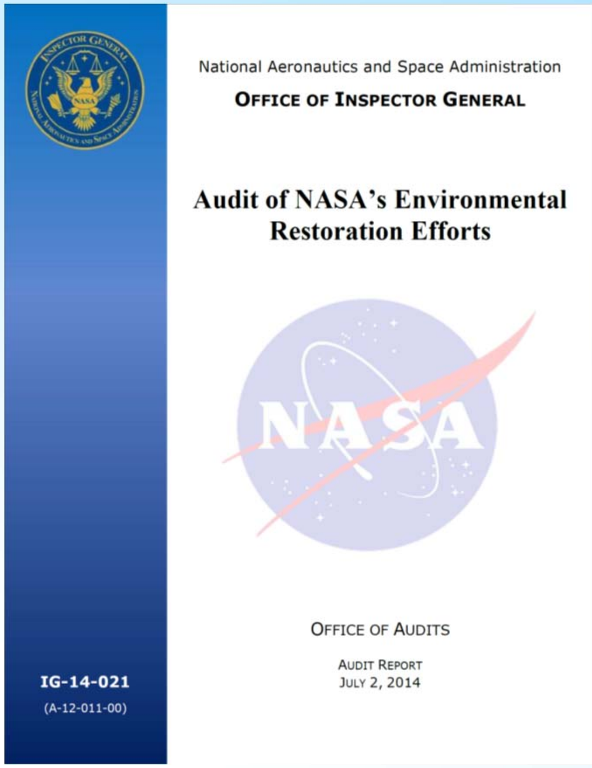
Precision Cleaning at KSC

- Vital for proper functioning of aerospace hardware
- Levels specified by KSC-C-123-J
  - 25A most stringent
- Verified by particle counting and non-volatile residue (NVR) analysis

Particulate Matter Contamination Levels			NVR Contamination Levels		Visible Contamination Levels	
Level	Particle Size Range µm (micrometer)	Maximum Number of Particles per 0.1 m^2	Level	Maximum NVR (mg/0.1 m^2)	Level	Definition
25	<5 5 to 15 >15 to 25 >25	Unlimited* 19 4 0	A	1.0	GC	Freedom from manufacturing residue, dirt, oil, grease, etc.

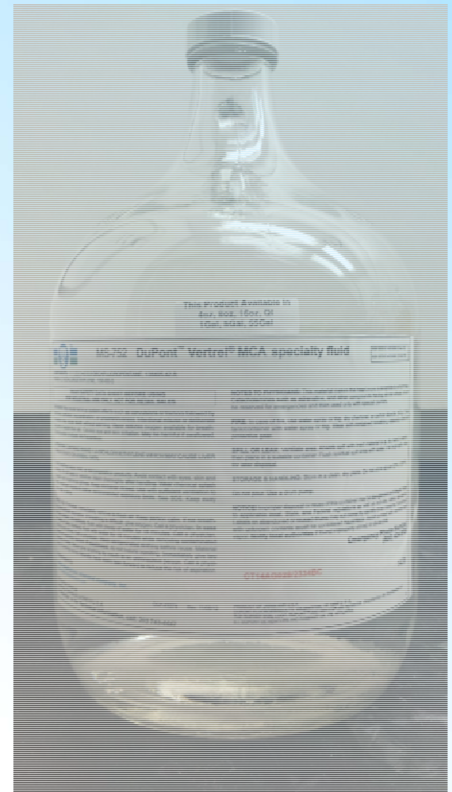
History and Legacy at KSC

- Have previously used halogenated solvents
  - Carbon tet, TCE, Freon
- No longer used due to health/regulatory issues
- Estimated $129M unfunded environmental liabilities



Current KSC Process

- Dual solvent process
  - » Cleaning – Vertrel MCA (DFP and *trans*-DCE)
  - » Analysis – HFE-7100
- Has led to at least two contamination sites
- DFP 20 year GWP = 4170 CO_2eq (CH_4 = 86)



Green Solvents Project Objective

Identify and evaluate environmentally benign cleaning technologies for space and aviation systems capable of cleaning to level 25A (NVR < 1.0 mg/ft^2) as per KSC-C-123J

- Other considerations
  - Toxicity
  - Flammability/LOX compatibility
  - Expense

Initial Research

- Greener solvents
  - Halogenated solvents intentionally avoided
  - 23 solvents initially tested; narrowed down to five
- Plasma
  - Used for surface activation, etching, polymer coating, etc.
- Supercritical carbon dioxide
  - Used for polymer processing, natural product extraction, aerogel production, etc.

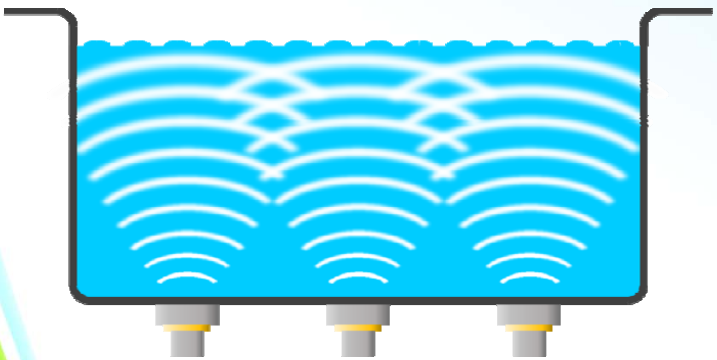
Experimental Approach

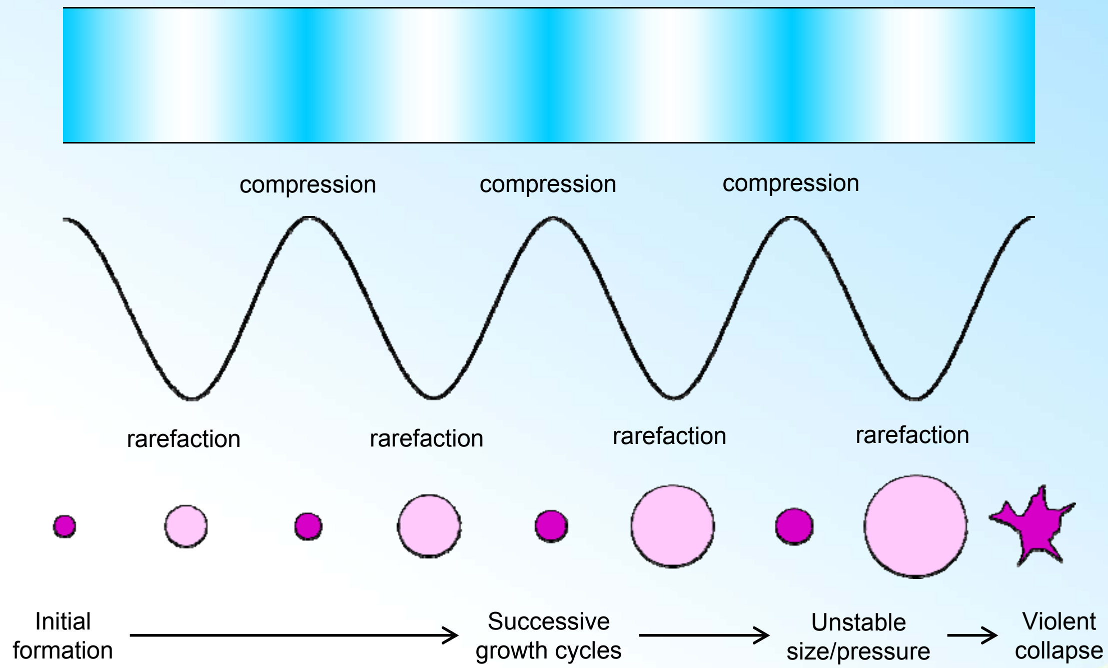
- Small parts w/ complex geometries
- Contaminated with individual contaminants or a "witch's brew" of all five
  - Krytox 240AC
  - Braycote 601EF
  - Mil-PRF-83282
  - Mil –H-5606
  - Dioctyl sebacate
- Gravimetric analysis used to calculate cleaning efficiencies

$$\frac{m_2 - m_3}{m_2 - m_1} * 100\% = \%E$$

m_2 = contaminated mass
m_3 = experimentally cleaned mass
m_1 = initial mass

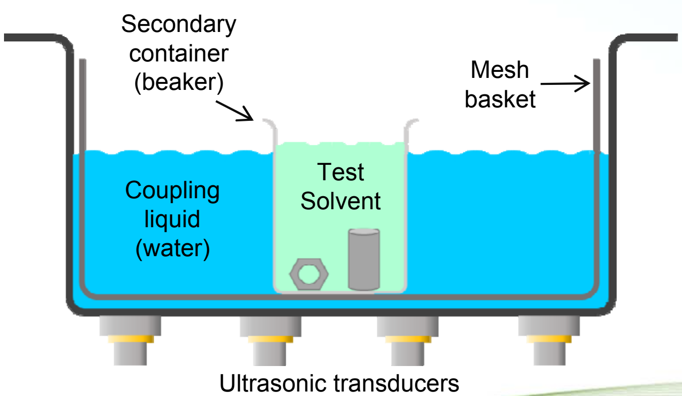
Ultrasonic Solvent Cleaning - Introduction





Ultrasonic Solvent Cleaning - Method

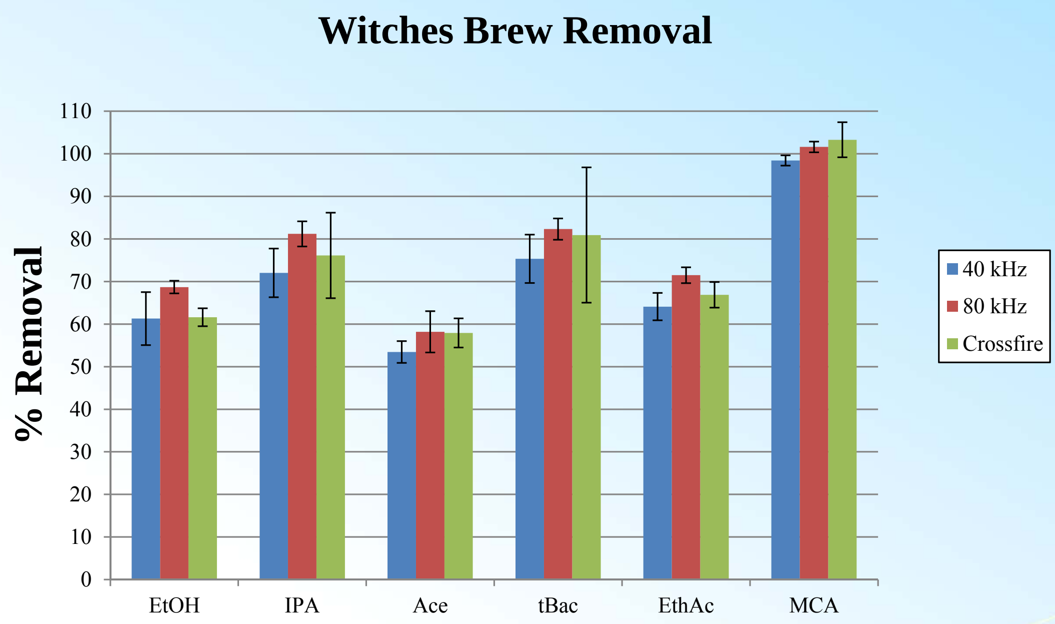
- Ultrasonic solvent cleaning parameters:
  - » Solvents tested: ethanol, 2-propanol, ethyl acetate, tert-butyl acetate, acetone
  - » Ultrasound frequency: 40 kHz, 80 kHz, Crossfire (alternating between 40 & 80 kHz)



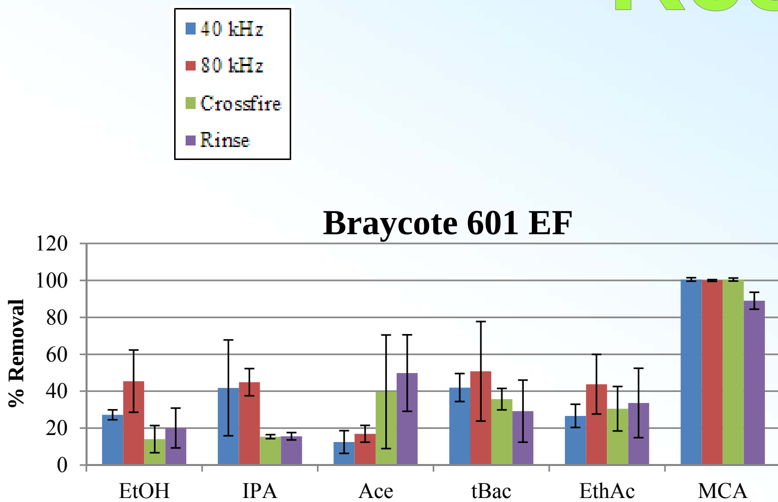
Sonicated for 5 min. in 50 ml of solvent

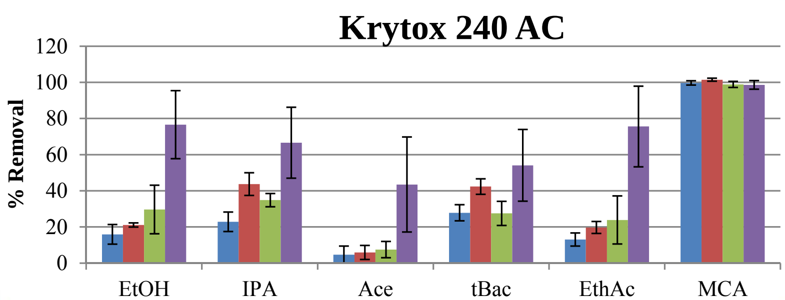
Ultrasonic Solvent Cleaning - Results

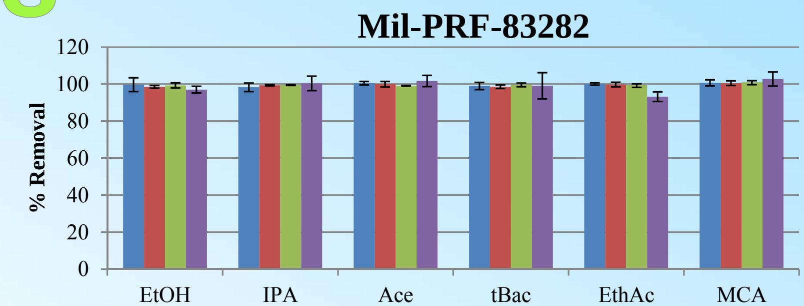
- None of the solvents matched Vertrel
- Frequency had little effect
- Ultrasonic agitation did not produce adequate cleaning

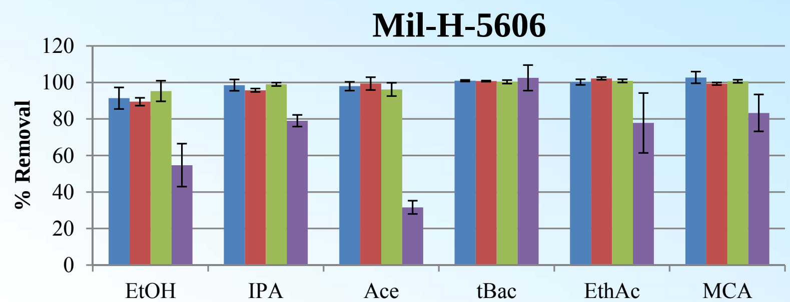


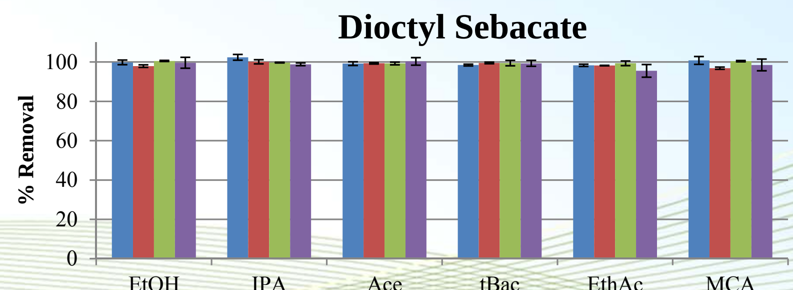
Ultrasonic Solvent Cleaning - Results











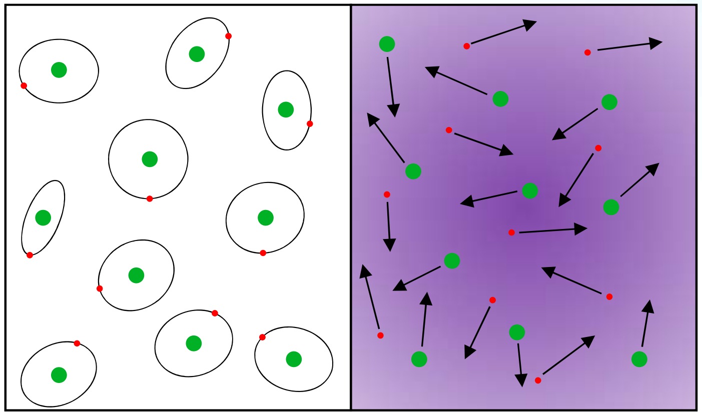
Ultrasonic Solvent Cleaning - Conclusions

- Hydraulic fluids (hydrocarbon-based) were able to be fully removed by ultrasonic solvent cleaning.
  - No significant differences in solvent selection or ultrasound frequency were observed.
- Fluorinated greases were not effectively removed.
  - Ultrasonic solvent cleaning did not improve contaminant removal, in general.
  - No clear trends based on either solvent or frequency were observed
- Samples passed both KSC and third party NVR analysis

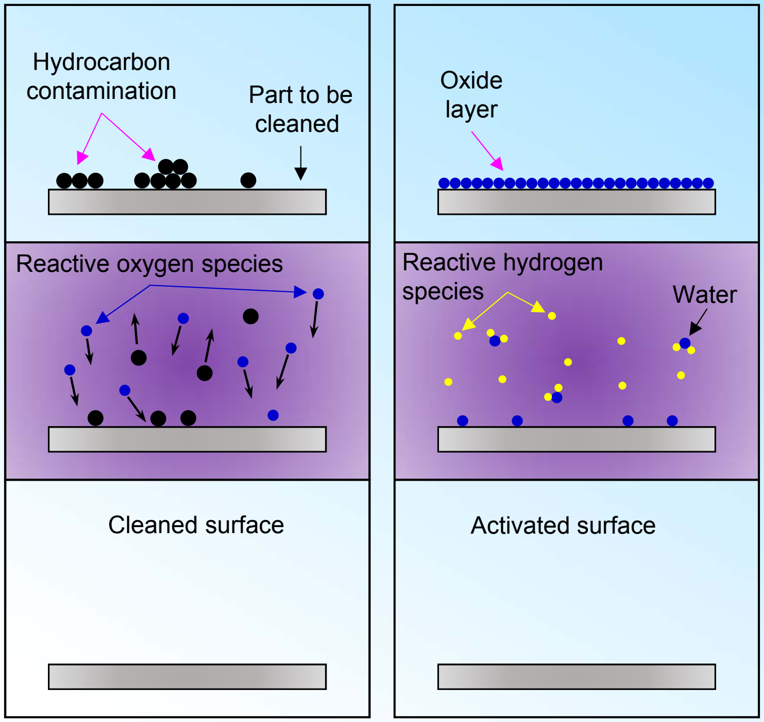
Cleaning parameters	Witch's brew deposited, mg	Witch's brew removed, mg	KSC NVR, mg	PFC NVR, mg
EtOH, 5 min, 80 kHz	13.61	13.69	-0.08	0.58
	11.93	12.21	-0.28	0.25

Plasma Cleaning - Introduction

- Ionized gas
  - Sun, lightning, St. Elmo's fire
- Creates high energy/highly reactive species



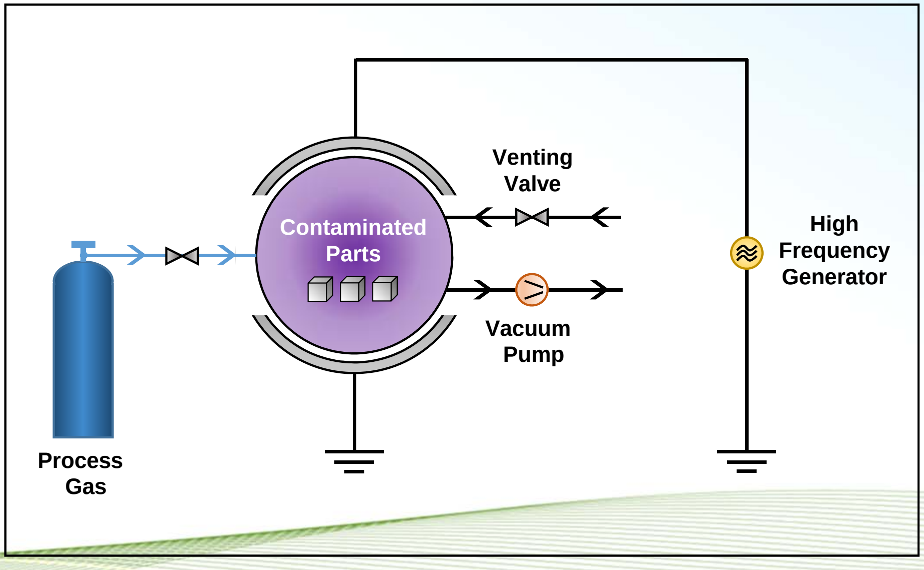
Gas state   Plasma state



Oxygen plasma cleaning process   Hydrogen plasma cleaning process

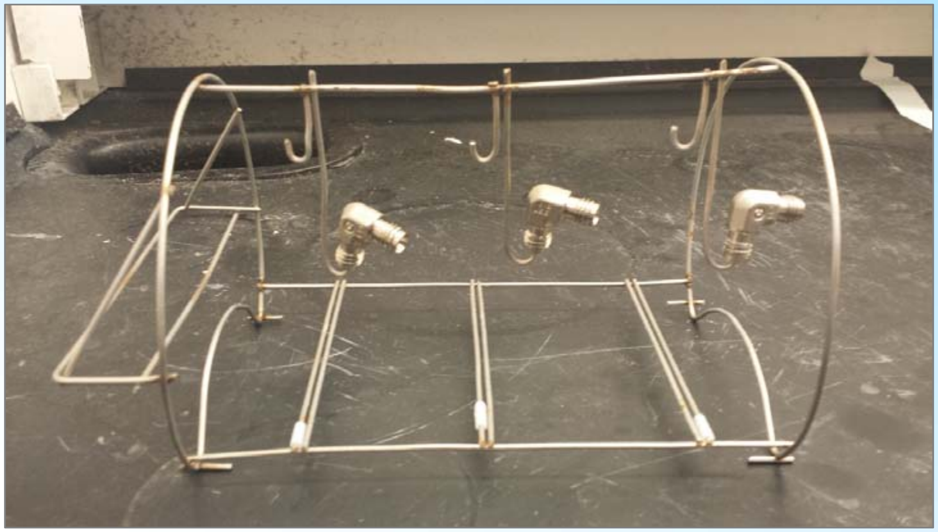
Plasma Cleaning - System

- Diener Pico system
- 40kHz, 200W plasma generator
- Three supply gas connections



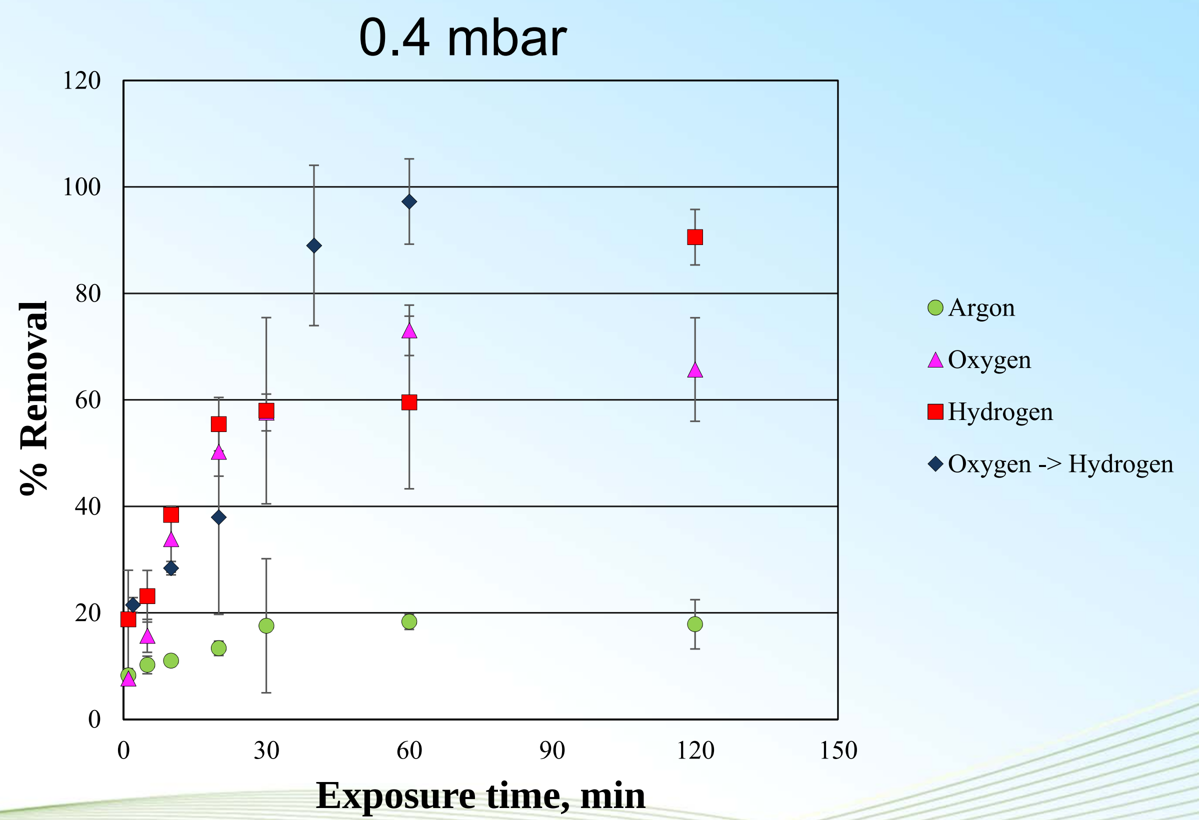
Plasma Cleaning – Method

- Plasma cleaning parameters:
  - Pressure: 0.1 & 0.4 mbar
  - Exposure time: 5 - 120 min
  - Gas type: argon, hydrogen, nitrogen, oxygen



Plasma Cleaning - Results

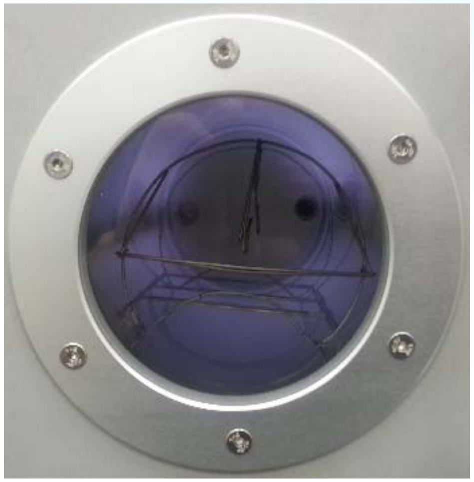
- Cleaning time has large influence
- Reactive gases had better results



Pressure Effect on Plasma

- Plasma generated at 0.4 mbar was not as vibrant as 0.1 mbar

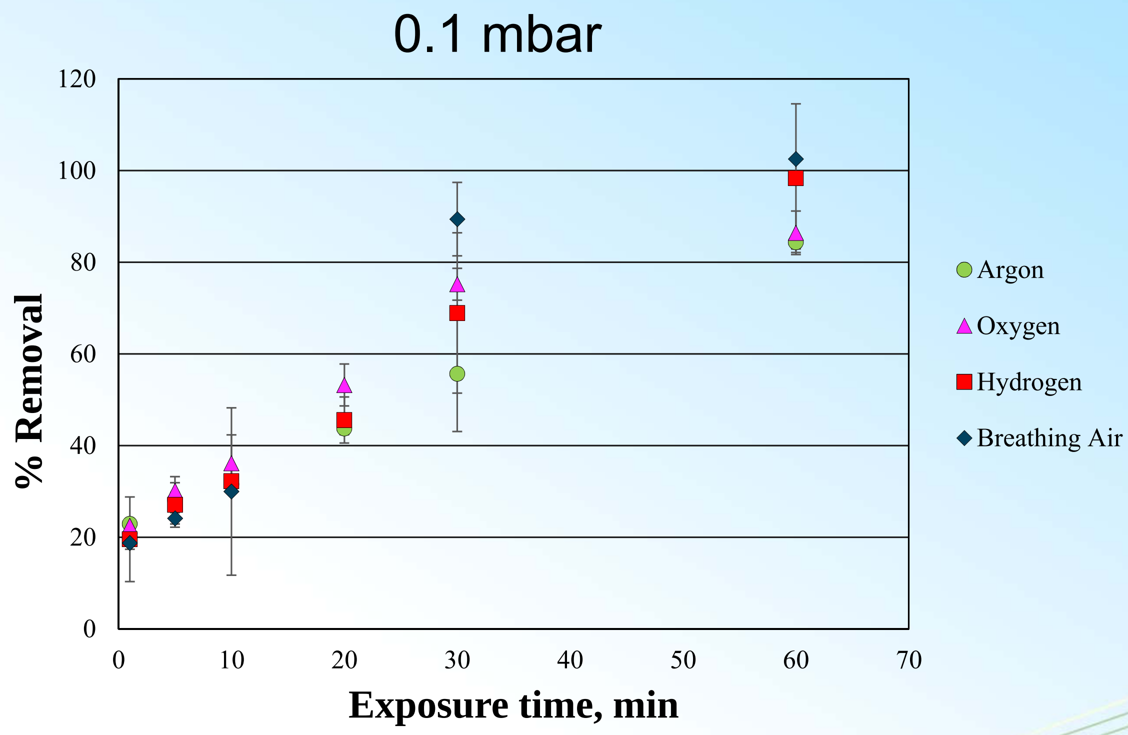
0.8 mbar



0.1 mbar

Plasma Cleaning - Results

- Time had significant effect on cleaning %
- All gases improved at lower pressure
- Breathing air performed extremely well



Plasma Cleaning - Conclusions

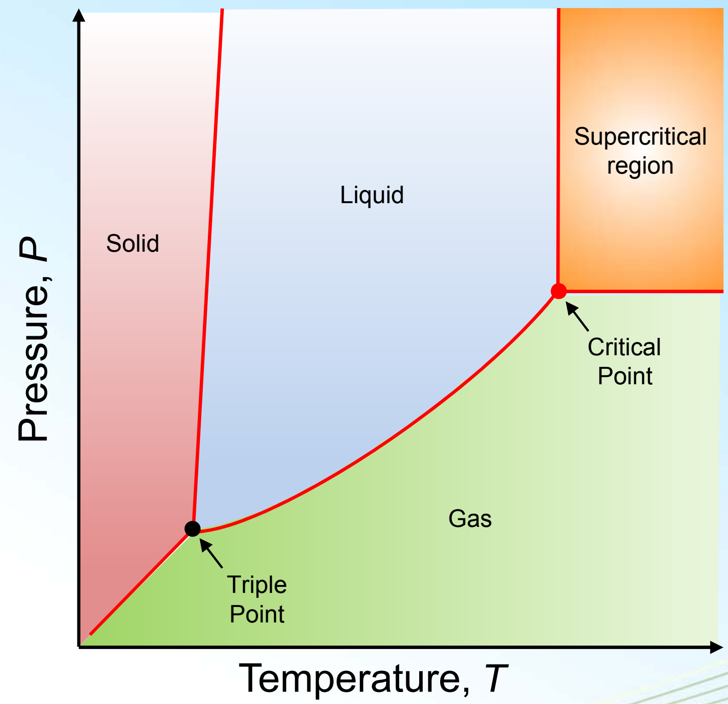
- Lower pressures are more effective for contaminant removal.
  - Higher pressures are suspected of ‘quenching’ the plasma formation.
- Breathing air and hydrogen were effective process gases removing approximately 100% of the deposited contaminant in 60 min.
- Samples failed KSC NVR analysis but passed third party analysis

Cleaning parameters	Witch’s brew deposited, mg	Witch’s brew removed, mg	KSC NVR, mg	PFC NVR, mg
Air, 60 min, 0.1 mbar	13.89	12.89	1.00	0.30
	16.37	13.81	2.56	0.40

$SCCO_2$ Cleaning - Introduction

- Liquid/gas hybrid
- Formed above P_c and T_c (7.39 MPa, 31.1 °C for CO_2)
- Solvent power can be tuned by adjusting P and T
- Co-solvents can be used to increase solvent power
- This process *does not* generate CO_2

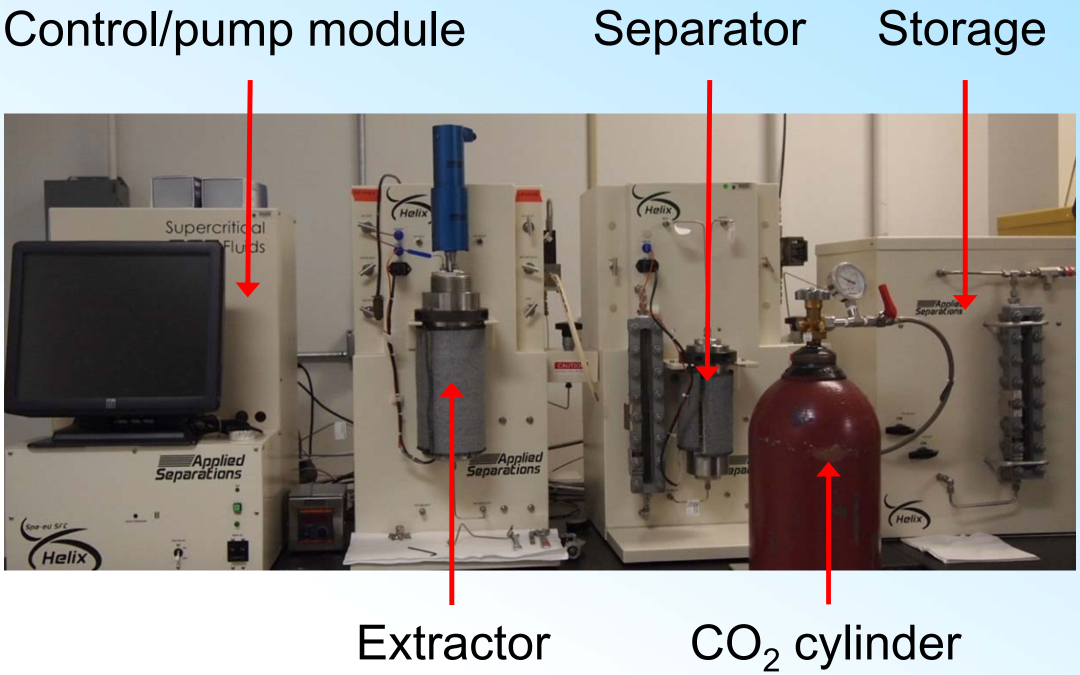
Typical phase diagram



$SCCO_2$ Cleaning - Method

- Extractor parameters:
  - Temperature: 35, 50, 75, 100 °C
  - Pressure: 82.8, 138, 276, 414 bar
  - Exposure time: 5, 30, 45, 60 min
  - Impeller speed: 0, 500, 750, 1000 rpm

Sample basket

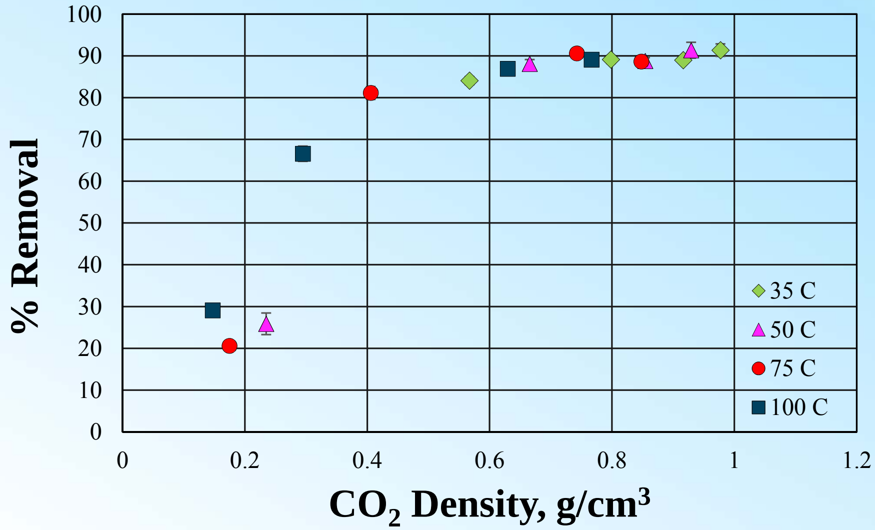


Helix laboratory-scale system from Applied Separations

$SCCO_2$ Cleaning - Results

- Increase % removal
  - Increase pressure
  - Decrease temperature
- No effect on % removal
  - Impeller speed
  - Exposure time

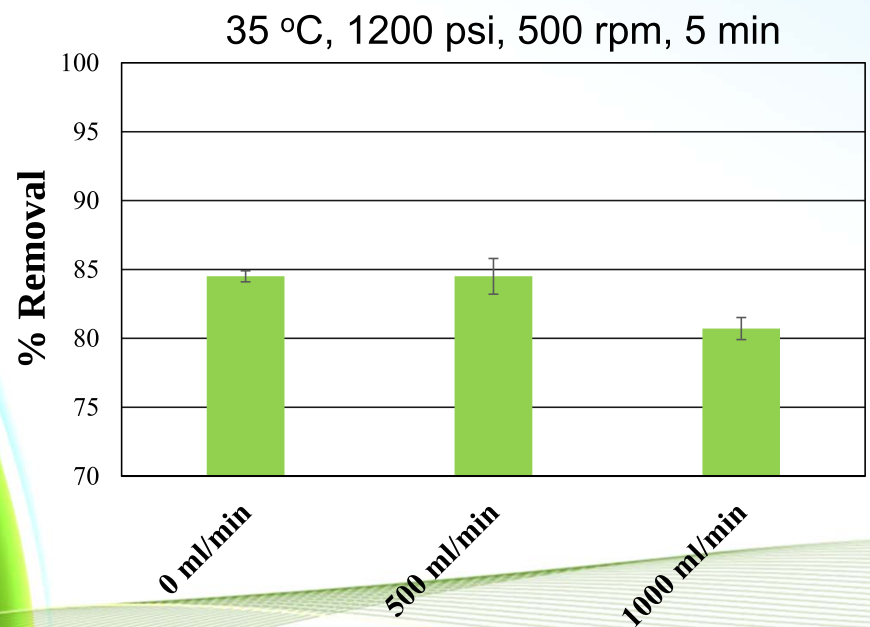
Time, min	Pressure, psi	Temperature, °C	Impeller Speed, rpm	Average % Removal	Standard Deviation, %
5	1200	35	0	84.1	1.0
5	2000	50	500	88.1	1.0
5	4000	75	750	90.6	0.7
5	6000	100	1000	89.1	1.2
30	2000	35	750	89.1	0.9
30	1200	50	1000	25.9	2.6
30	6000	75	0	88.6	0.8
30	4000	100	500	86.9	1.2
45	4000	35	1000	89.0	0.3
45	6000	50	750	91.3	1.9
45	1200	75	500	20.6	0.1
45	2000	100	0	66.6	1.8
60	6000	35	500	91.4	1.5
60	4000	50	0	88.8	0.8
60	2000	75	1000	81.1	1.5
60	1200	100	750	29.1	1.2

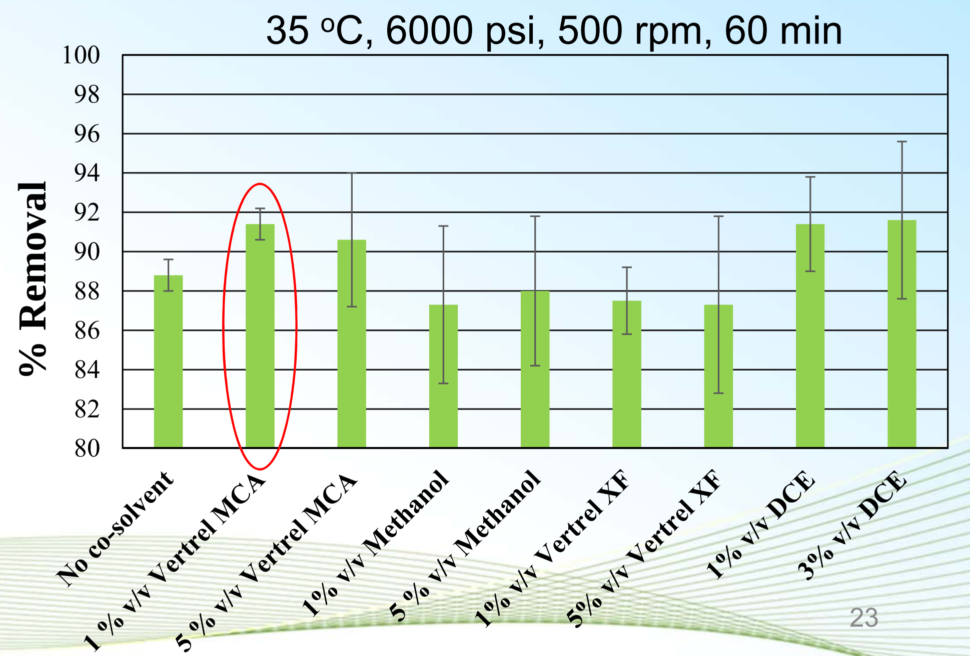


- CO_2 density, a function of P/T, correlates well with % removal
- Densities > 0.7 g/cm^3 removed ≈ 90% of the contaminants

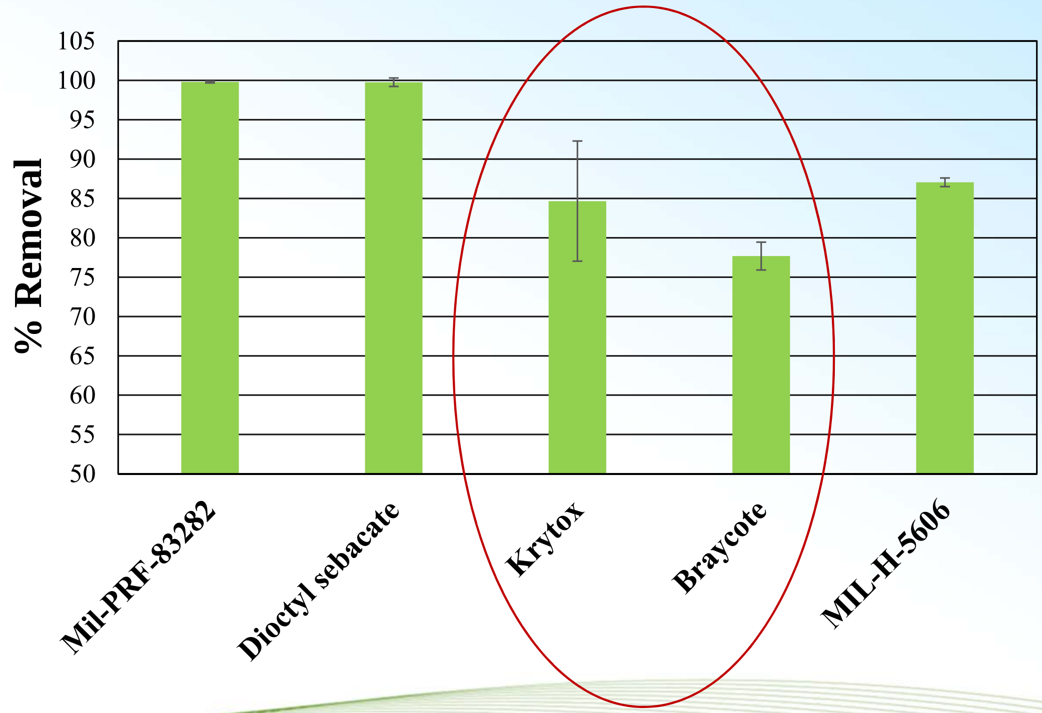
SCCO2 Cleaning - Results

- Continuous flow did not significantly effect % removal
- Only 1% v/v Vertrel MCA showed a significant improvement in % removal

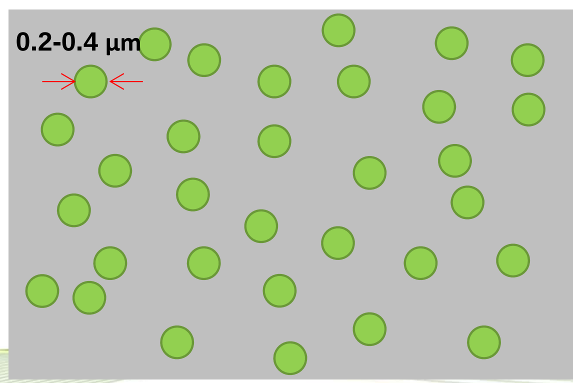


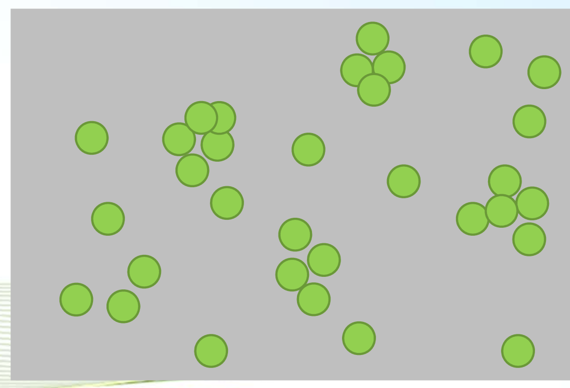


$SCCO_2$ Individual Contaminant Analysis



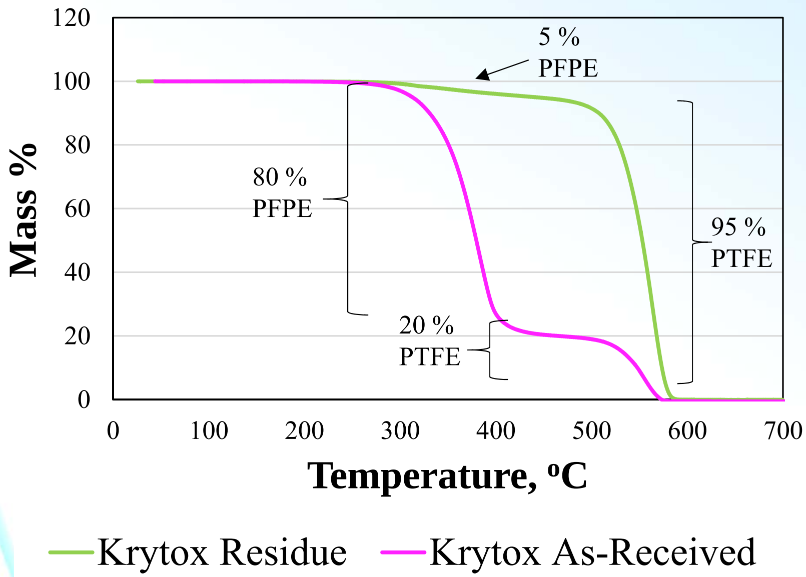
Residual Contaminant Analysis

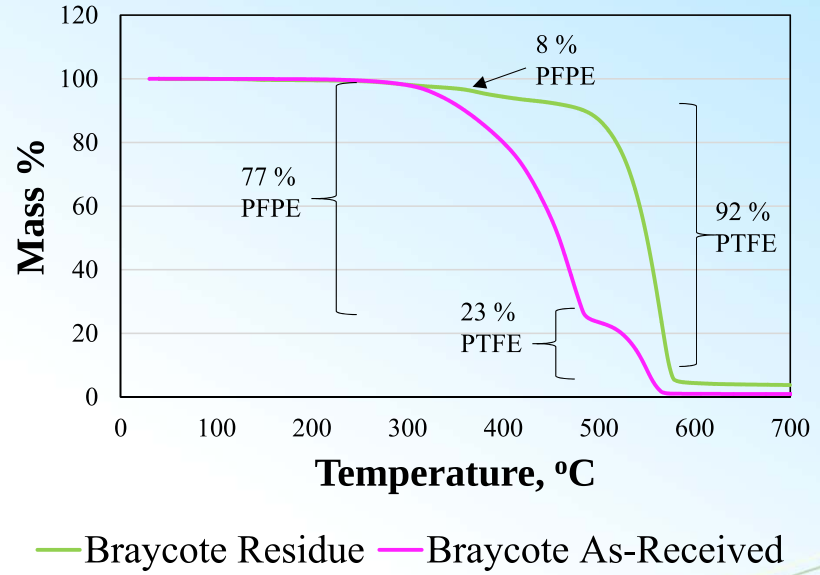




System Parts after Extraction of Krytox 240 AC

Residue Analysis by TGA





$SCCO_2$ Cleaning - Conclusions

- Effective at removing hydrocarbon and fluorinated greases
- Ineffective at removing particles
- Density is the critical parameter rather than pressure or temperature individually
- Neither co-solvents nor continuous flow reactions improved cleaning efficiencies
- Both samples failed KSC NVR analysis, however one passed third party analysis

Cleaning parameters	Witch's brew deposited, mg	Witch's brew removed, mg	KSC NVR, mg	PFC NVR, mg
Batch, 6000 psi, 35°C, 60min	11.70	9.60	2.10	0.93
	12.42	9.80	2.62	2.36

Technology Comparison

	Toxicity	Cleaning	LOX Compatible	Environ. Impacts	Flammability	Scalability	Upfront Costs	Lifetime Costs
Vertrel MCA								
Alternative Solvents								
Plasma								
Supercritical CO_2								

- All three technologies are able to be scaled up.
  - Large scale systems are commercially available for solvent and plasma cleaning.
  - Custom system design is necessary to scale up $SCCO_2$ cleaning.

Future work

- Explore plasma's ability to activate/passivate metals
- Investigate ways to remove particles in $SCCO_2$
  - Electrokinetics
  - Mechanical agitation
  - Sonic agitation
  - Surfactants
- *In-situ* contamination monitoring
- Next-level scale up testing
- In-depth economic analysis
- Full-scale implementation

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- Team Members:
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  - Dr. Heather Grandelli
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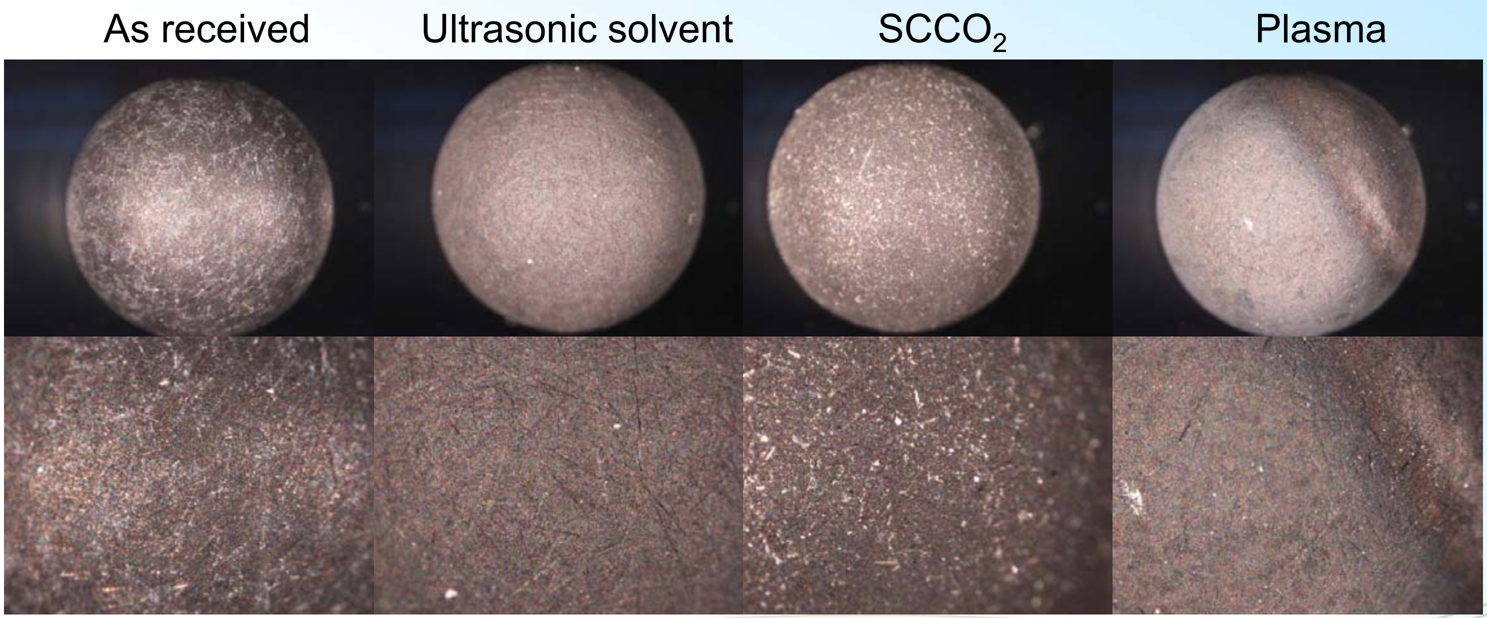
Thank you for your attention!

Soft Goods Compatibility

- 4 materials tested: Neoprene, Buna-N, Teflon, and Viton
- Analyzed for changes in hardness, mass, diameter, and circularity



Neoprene pre- and post-exposure.

Soft Goods Compatibility – Summary

- Solvents and plasma decrease mass
- $SCCO_2$ adds mass
- Generally, shape is not affected
- No overall trends in Δ hardness

Type of Cleaning Test	Material	Durometer Hardness Before	Durometer Hardness After	Mass Δm, g	Diameter Δd, in	Circularity Δc
Ultrasonic Solvent	Buna-N	80A	83A	-0.00216	neg	neg
	Viton	82A	87A	-0.00023	neg	neg
	Teflon	66D	67D	-0.00037	0.0012	0.0009
	Neoprene	86A	82A	-0.00084	neg	neg
$SCCO_2$	Buna-N	81A	80A	0.00199	neg	neg
	Viton	84A	81A	0.00817	0.0014	neg
	Teflon	66D	63D	0.00007	0.0008	0.0008
	Neoprene	82A	80A	0.00119	neg	neg
Plasma	Buna-N	86A	87A	-0.00258	neg	neg
	Viton	85A	84A	-0.00269	neg	neg
	Teflon	66D	65D	-0.01986	neg	0.0015
	Neoprene	88A	82A	-0.00367	0.0013	neg

Third Party Verification Summary

Process Description	Test method cleaning parameters	Witch's brew deposited, mg	Witch's brew removed by cleaning, mg	KSC determined NVR	PFC determined NVR
"True cleaned"	n/a	0	n/a	0	0.33
"True cleaned"	n/a	0	n/a	0	1.33
Contaminated but not cleaned	n/a	11.03	n/a	11.03	4.7
Contaminated but not cleaned	n/a	11.57	n/a	11.57	4.31
Cleaned by Ultrasonication	Ethanol, 5 min, 80 kHz	13.61	13.69	-0.08	0.58
Cleaned by Ultrasonication	Ethanol, 5 min, 80 kHz	11.93	12.21	-0.28	0.25
Cleaned by $SCCO_2$	Batch process, 6000 psi, 35°C, 60 min	11.7	9.6	2.1	0.93
Cleaned by $SCCO_2$	Batch process, 6000 psi, 35°C, 60 min	12.42	9.8	2.62	2.36
Cleaned by plasma	Breathing air plasma, 60 min, 0.1 mbar, 100% power	13.89	12.89	1	0.3
Cleaned by plasma	Breathing air plasma, 60 min, 0.1 mbar, 100% power	16.37	13.81	2.56	0.4